Electronic spectroscopy of benzene and the fluorobenzenes by variable angle electron impact[a)]

Robert P. Frueholz,[b)] Wayne M. Flicker,[c)] Oren A. Mosher,[d)] and Aron Kuppermann

Arthur Amos Noyes Laboratory of Chemical Physics,[e)] California Institute of Technology, Pasadena, California 91125

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Electron-impact spectra of benzene and 11 fluorine-substituted derivatives have been obtained at impact energies of 75, 50, and either 25 or 30 eV, and scattering angles from 5° to 80°. Each molecule shows an absorption maximum at about 3.9 eV, corresponding to a singlet→triplet, $\pi \rightarrow \pi^*$, transition. In benzene, fluorobenzene, *o*- and *m*-difluorobenzene, and 1,3,5-trifluorobenzene, an additional singlet→triplet excitation was detected at about 5.7 eV. Three singlet→singlet transitions analogous to the 4.90, 6.20, and 6.95 eV benzene excitations are seen in each of the fluorine-substituted molecules. The more highly substituted compounds exhibit an additional singlet→singlet transition, which we designate as the *C* band system, that is most clearly observed in the hexafluorobenzene spectrum, where it has a peak at 5.32 eV. We briefly discuss the effects on relative transtion intensities due to the different molecular symmetries of the various fluorobenzenes. We also report numerous superexcited states for each molecule studied.

I. INTRODUCTION

Extensive experimental and theoretical work has been performed in an attempt to understand the electronic spectroscopy of benzene and its derivatives, especially the halogenated derivatives. Historically, the bands resulting from excitation to the lowest singlet state of benzene represented the first extensive and clearcut example of electronic transitions forbidden by symmetry selection rules; their interpretation was achieved using vibronic selection rules.[1] In order to gain more information about the electronic spectroscopy of the simplest halogenated derivatives of benzene, we have applied the experimental technique of low energy, variable angle, electron-impact spectroscopy[2] in the present study to all possible fluorine-substituted benzenes except 1,2,3-trifluorobenzene.

The specific goals of this research were to locate singlet→triplet electronic transitions, to determine the shape of their Franck–Condon envelopes, and to investigate systematically the effects of fluorine substitution on the electronic transitions of the π-electron ring. Accurate triplet state energies allow a determination of singlet–triplet energy splittings that may be a factor in determining the value of the rate of intersystem crossing.[3] The maximum intensity locations (generally corresponding to the vertical transition energies) are useful for comparison with theoretical values. In addition, high-quality electronic band shapes of singlet→triplet transitions are important for analysis of photochemical electronic energy transfer experiments.[4–10] Investigation of the spectra of the fluorobenzenes is also inherently interesting because the replacement of hydrogen by fluorine in the benzene system should perturb both σ and π orbitals.[11,12] Changes in transition energies, with varied fluorine substitution, will reflect the different effects of fluorine substitution on the ground and excited states.

In this paper, we report results obtained from the 3 to 18 eV energy-loss region of benzene; fluorobenzene; *o*-, *m*-, and *p*-difluorobenzene; 1,3,5- and 1,2,4-trifluorobenzene; 1,2,3,4-, 1,2,4,5-, and 1,2,3,5-tetrafluorobenzene; pentafluorobenzene; and hexafluorobenzene. In Sec. II, we summarize the previous experimental and theoretical studies performed on the fluorobenzenes, and in Sec. III we describe the present experiment. Results and their discussion are presented in Sec. IV. We conclude with a brief summary and statement of the conclusions in Sec. V.

II. SUMMARY OF BENZENE SPECTROSCOPY AND OF PREVIOUS FLUOROBENZENE STUDIES

The spectroscopy of the fluorobenzenes is intimately related to that of the parent molecule (benzene). The highest occupied molecular orbitals in benzene have the symmetries $e_{1g}(\pi_2, \pi_3)$, $e_{2g}(\sigma)$, and $a_{2u}(\pi_1)$, in the order of increasing ionization potential.[11] Over the energy-loss region 3.0 to 8.5 eV, the gross features of the benzene spectrum include three singlet→singlet transitions, resulting from the excitation of an e_{1g} electron to an $e_{2u}(\pi^*)$ orbital, occurring at energy losses of about 4.90, 6.20, and 6.95 eV.[13] The first and third singlet→singlet excitations can be assigned as the symmetry-forbidden $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ and the symmetry-allowed $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ excitations.[1,14]

The identity of the second singlet→singlet transition is still somewhat uncertain. The most probable assignment appears to be the symmetry-forbidden, $\pi \rightarrow \pi^*$, $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ excitation.[14,15] However, the low angle electron-impact spectra of Lassettre *et al.*[13] and Doering[16] indicate the possibility of two transitions occurring

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b) Work performed in partial fulfillment of the requirements for the Ph. D. Degree in Chemistry at the California Institute of Technology.

c) Present address: Harvard–MIT Division of Health Sciences and Technology, Harvard Medical School, Boston, MA 02115.

d) Present address: Eagle Machinery Co. Ltd., 948 88th Avenue, Oakland, CA 94621.

e) Contribution No. 5800.

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in this region. On the basis of the variation of peak intensities with scattering angle, Lassettre *et al.*[13] suggested that vibronic peaks occurring at 6.31, 6.41, and 6.53 eV (the first being the most intense) belonged to an excitation other than the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$, which they found at 6.20 eV. Further evidence in support of this suggestion comes from multiphoton ionization experiments.[17] In the multiphoton ionization spectrum, vibronic peaks were observed at transition energies including 6.33, 6.42, and 6.53 eV, with the 6.33 eV peak being the most intense of all transitions observed. No transition was observed at 6.20 eV, which is consistent with the fact that the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ transition (which would be a two-photon resonance intermediate in the three-photon ionization) is forbidden by two-photon selection rules. The correlation between the results of these two different experimental techniques supports, very strongly, the existence of at least two electronic states of benzene in the excitation energy range of 6.2 to 6.7 eV. An additional $\pi \rightarrow \pi^*$ transition $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{2g}$, resulting from the excitation of an a_{2u} electron to the $e_{2u}(\pi^*)$ orbital predicted by theoretical studies[18,19] to occur in the region of the intense, 6.95 eV, $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ excitation, but such a transition has not yet been unambiguously identified.[14] It is possible that the excitation observed by Lassettre and co-workers[13] and by Johnson[17] is this $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{2g}$ transition.

Doering,[16,20] who has studied benzene via low energy, variable angle, electron impact, assigned three other transitions occurring at 3.89, 4.85, and 5.69 eV to singlet → triplet transitions. The first and third may be identified as $\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{1u}$ and $\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{2u}$ transitions,[18-20] while the second is believed to be the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^3E_{1u}$ excitation.[18,19]

The electronic spectroscopy of the fluorobenzenes has also received significant attention.[12,21-26] The observed transitions, in the 3.0 to 8.5 eV energy-loss region, are quite similar to those observed in benzene. Due to this similarity, these transitions are most easily discussed in terms of the benzene symmetry notation, even though it applies rigorously only to hexafluorobenzene. The lowest singlet → singlet excitation in the fluorobenzenes appears to be analogous to the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ transition in benzene. It has been studied optically by several authors.[12,21-23] The higher excited singlet → singlet transitions, apparently corresponding to the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ and $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ excitations of benzene, have been investigated by Sandorfy and co-workers.[24] Spin-forbidden transitions have also been studied, but to a lesser extent. Evans,[25] using the oxygen-perturbation technique, obtained the $S_0 \rightarrow T_1$ absorption spectrum of fluorobenzene, while Metcalfe *et al.*[26] investigated the $S_0 \rightarrow T_1$ absorption spectra of 11 fluorobenzenes using the same method. However, the accuracy of the $S_0 \rightarrow T_1$ absorption profiles and of the positions of the intensity maxima is limited in this technique because the $S_0 \rightarrow T_1$ transition is partially masked by the diffuse charge-transfer band of the aromatic contact complex. Photochemists have also studied these states indirectly using the triplet state-induced *cis–trans* isomerization of *cis*-2-butene and the triplet photosensitized phosphorescence of biacetyl.[7-10]

In addition to experimental interest in the excited electronic states of the fluorobenzenes, there have been several theoretical studies of their excitation energies.[27-35] Unfortunately, these calculations have been limited to applications of various semiempirical techniques. To our knowledge, no *ab initio* calculations have yet been performed on excited states of the fluorobenzenes. While the available semiempirical excitation energies are generally within 1 eV of the experimental values, they are consistently below those values. As substitution is increased, the semiempirical calculations predict a monotonic decrease in excitation energy of a given transition.[30,35] This is not consistent with the observed experimental results.[12,24,26] Duke *et al.*[35] explain this shortcoming of the calculations as the result of an unrealistic lowering of the energy of the π^* orbitals with fluorine substitution. While the semiempirical calculations performed on the fluorobenzenes are limited in scope, high-quality *ab initio* configuration interaction (CI) calculations have been performed on benzene and its excited states by Hay and Shavitt.[18] Their detailed discussion of the transitions observed in the benzene spectrum is of value when considering the very similar transitions of the fluorobenzenes.

III. EXPERIMENTAL

The instrument used in these studies has been described in detail by Kuppermann and co-workers.[2] The spectrometer consists basically of a multistage electron gun, a hemispherical electrostatic energy monochromator, a flexible bellows scattering chamber which contains the target gas, an energy-loss analyzer identical to the monochromator, and a Spiraltron electron multiplier. Pulses from the multiplier are amplified and shaped, then counted with a 1024 channel scaler. In a typical experiment, the incident electron energy E_0 and the scattering angle of detection θ are both fixed, and the energy-loss spectrum is scanned repeatedly, usually for a period of 4 to 8 h. The method of data reduction used to obtain both elastic and inelastic differential cross sections (DCS's) has also been described previously.[36]

The benzene and fluorobenzene used in these studies were obtained from Matheson, Coleman and Bell. The benzene sample was A.C.S. reagent grade with a boiling point range of 1 °C, while the fluorobenzene used also had a stated boiling point range of 1 °C. 1,3,5- and 1,2,4-trifluorobenzene were obtained from PCR, Inc. with stated minimum purities of 97%. All other chemicals were obtained from the Aldrich Chemical Company. *m*-Difluorobenzene and 1, 2, 3, 5-tetrafluorobenzene had stated minimum purities of 97% and 99+%, respectively, while the other compounds had stated minimum purities of 98%. All samples were subjected to several freeze–pump–thaw cycles prior to use.

Spectra were taken for these molecules at impact energies of 75, 50, and either 25 or 30 eV. The energy-loss range scanned was 3.0 to 18 eV. Sample pressures in the scattering chamber ranged from 2 to 8 mTorr, as indicated by an uncalibrated Schulz–Phelps ionization gage. The instrumental resolution, as determined from

TABLE I. Transition energies of the fluorobenzenes.

Molecule	Transition energies (eV)[a]											
	Singlet → triplet				Singlet → singlet[b]							
	$(\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{1u})^c$		$(\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{2u})^c$		$(\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u})^{c,d}$		C band		$(\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u})^c$		$(\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u})^c$	
Benzene	3.90	(3.89)[e]	5.59	(5.69)[e]	4.80	(4.89)[e]			6.25	(6.2)[e]	6.95	(6.95)[e]
Fluorobenzene	3.90	(3.88)[f]	5.72		4.78				6.23		6.99	
o-Difluorobenzene	3.92	(3.88)[f]	5.67		4.76				6.22		7.02	
m-Difluorobenzene	3.91	(3.84)[f]	5.72		4.79				6.17		6.96	
p-Difluorobenzene	3.85	(3.77)[f]			4.67				6.18		7.02	
1,3,5-Trifluorobenzene	3.95	(3.92)[f]	5.62		4.87				6.20		6.94	
1,2,4-Trifluorobenzene	3.89	(3.82)[f]			4.72				6.20		7.04	
1,2,3,4-Tetrafluorobenzene	3.95	(3.82)[f]			4.85		~6.0[g]		6.43		7.21	
1,2,3,5-Tetrafluorobenzene	3.93	(3.91)[f]			4.79		[6.5][h]		6.2(±0.1)		7.10	
1,2,4,5-Tetrafluorobenzene	3.93	(3.73)[f]			4.69		[6.4][h]		6.3(±0.1)		7.25	
Pentafluorobenzene	3.90	(3.88)[f]			4.79		5.85		6.36		7.12	
Hexafluorobenzene	3.86	(3.81)[f]			4.80		5.32	(5.31)[i]	6.36		7.10	

[a]These are the locations of intensity maxima to an accuracy of ± 0.05 eV, unless otherwise indicated.
[b]Our excitation energies for singlet → singlet transitions are in good agreement with values obtained optically; see Refs. 12 and 24.
[c]The symmetry designations correspond to transitions for benzene.
[d]According to Doering's results,[16] this feature consists of two overlapping transitions: a singlet → singlet transition with maximum intensity at 4.89 eV and a singlet → triplet transition which peaks at 4.85 eV.
[e]Excitation energies in parentheses were obtained from the electron-impact studies (Ref. 16).
[f]Excitation energies in parentheses were obtained from oxygen perturbation optical spectra (Ref. 26).
[g]Appears as broadening on the low energy side of 6.43 eV feature.
[h]Location approximate.
[i]Reference 40.

the full width at half-maximum (FWHM) of the elastic peak, was set electron optically in the range 0.10 to 0.16 eV.

IV. RESULTS AND DISCUSSION

A. Transitions below 8 eV

Table I summarizes the principal transition energies in the 3.0 to 8.5 eV energy-loss region obtained in the present experiments for benzene and the 11 fluorobenzenes studied. Figures 1 and 2 display the high angle spectra for all of these molecules.[37] These spectra were obtained at either 25 or 30 eV impact energy. The electronic band shapes do not change significantly between these two impact energies and can be compared with each other. Figure 3 displays the spectra of the three difluorobenzene isomers at 50 eV impact energy and 20° scattering angle, while Fig. 4 presents the corresponding spectra of 1,3,5- and 1,2,4-trifluorobenzene. Figure 5 shows those of the three tetrafluorobenzenes. Both elastic and inelastic DCS curves for selected fluorobenzenes are displayed in Figs. 6–11.

In the energy-loss region from 3.0 to 8.5 eV, the spectra of the mono-, di-, and trifluorinated molecules are quite similar to that of benzene. Each molecule possesses three transitions at approximately 4.8, 6.2, and 7.0 eV, which appear to be equivalent to the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$, $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$, and $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ excitations in benzene. Each of these transitions possesses a differential cross section which is forward-peaked (see Figs. 6–8). This DCS behavior is characteristic of singlet → singlet transitions and is consistent with the commonly accepted nature of these transitions.[24,38] The DCS curves for the transitions occurring at about 4.8 eV are generally less forward peaked than those of the higher singlet → singlet transitions. This angular dependence is probably due to the presence of an underlying triplet state, as is the case in benzene where the second triplet overlaps the lowest-lying spin-allowed transition.[16] (In our benzene spectra, the second singlet → triplet transition reported by Doering[16,20] was not distinguishable from the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ transition.)

Each of the six fluorinated molecules thus far considered has a transition occurring at about 3.9 eV. These transitions display essentially isotropic differential cross sections as a function of angle (Figs. 6–8), and their intensity relative to the singlet → singlet transitions just described increases as the impact energy decreases. This behavior is characteristic of singlet → triplet transitions, in agreement with previous assignments.[26] These excitations appear to be analogous to the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{1u}$ transition observed in the benzene spectrum. In fluorobenzene, *o*- and *m*-difluorobenzene, and 1,3,5-trifluorobenzene, an additional weak transition was observed at about 5.7 eV. It was not possible to obtain reliable DCS values for this feature, due to its weakness and overlap with the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ excitation. However, the fact that it appeared principally in high-angle spectra, and increased in intensity relative to the singlet → singlet transitions as the impact energy decreased, is consistent with a singlet → triplet assignment. These transitions appear to be analogous to the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^3B_{2u}$ excitation in benzene which occurs at 5.69 eV.[16,18] The fact that this feature was not observed in the *p*-difluorobenzene and 1,2,4-trifluorobenzene spectra indicates that either its relative intensity is significantly weaker for these molecules or that the transition has shifted to higher energies. If the latter is the case, we estimate that the transition energies are higher than 5.9 eV. This is the onset of the much more intense $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ tran-

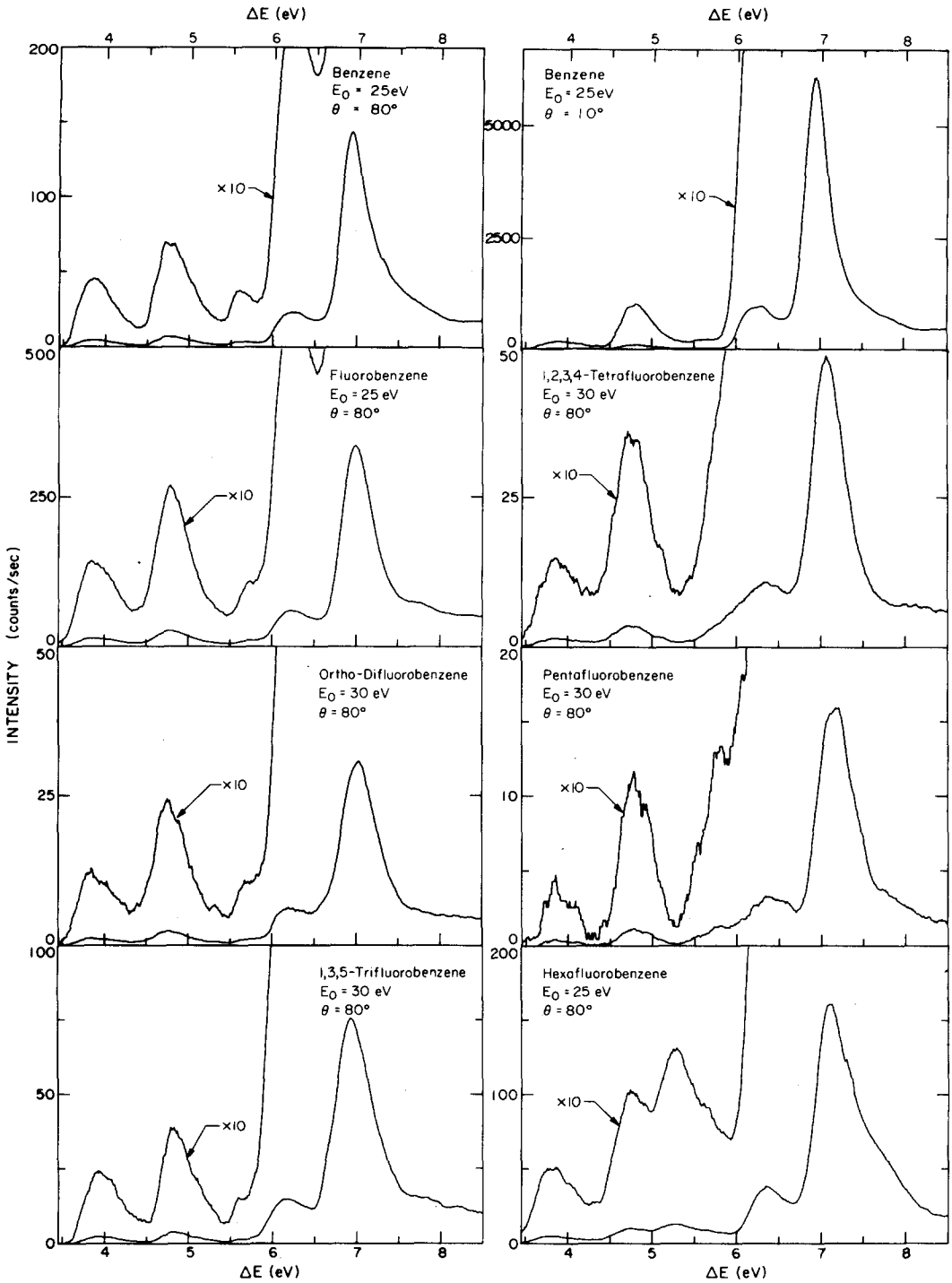

FIG. 1. Electron-impact energy-loss spectra of benzene and six fluorine-substituted derivatives in the 3.4 to 8.5 eV energy-loss region. Typical experimental parameters for these spectra and those presented in later figures are as follows: sample pressures ranging from 2 to 8 mTorr as measured with an uncalibrated Schulz–Phelps ionization gauge, incident electron beam currents of approximately 50 nA, and resolution in the range 120 to 160 meV FWHM.

sition, which would obscure weak features whose strengths are comparable to those observed in fluorobenzene and the other di- and trifluorobenzenes.

The electron-impact spectra of the tetra-, penta-, and hexafluorobenzenes are quite similar to the spectra of the less substituted fluorobenzenes. In the spectra of each of these molecules, the lowest energy transition observed occurs at about 3.9 eV. This is again a singlet → triplet excitation displaying, characteristically, a nearly isotropic DCS at both high and low impact energies (see Figs. 9–11). The excitation analogous to the third singlet → triplet transition of benzene is not detected in these molecules, due in part to the emergence of an additional singlet → singlet excitation, which will be discussed shortly. In hexafluorobenzene, a transition is seen at 5.71 eV, which might seem to be due to the third singlet → triplet excitation. A small peak at this energy

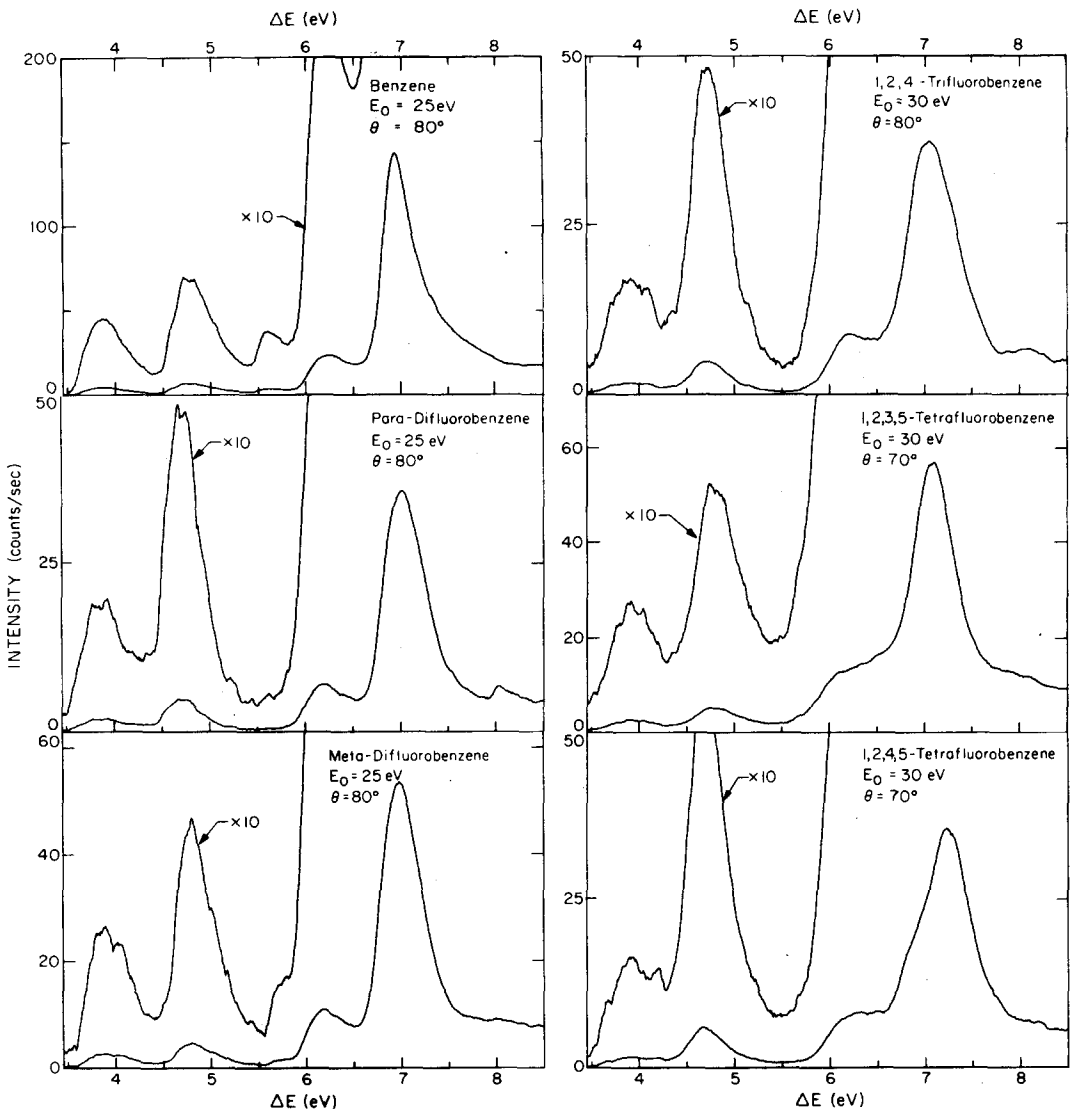

FIG. 2. Electron-impact energy-loss spectra of benzene and five fluorine-substituted derivatives. Experimental conditions are as in Fig. 1.

loss, superimposed on the underlying singlet → singlet feature, is apparent in several spectra; however, it is seen at both high and low angles with approximately equal relative intensity with respect to the singlet → singlet intensities, which precludes its assignment as a spin-forbidden transition. This 5.71 eV transition may be due instead to a small amount of impurity.

The three singlet → singlet transitions analogous to those in benzene are still present at similar energy losses in the tetrafluorobenzenes, pentafluorobenzene, and hexafluorobenzene. The DCS curves of these transitions are all forward peaked, which is consistent with the singlet → singlet nature of these excitations. In addition to these transitions, another feature emerges in the 5–6 eV region of the spectra. This new feature is clearly visible in the hexafluorobenzene spectrum, with an intensity maximum occurring at 5.32 eV. We designate this transition the *C* band system, for ease of reference.[39] Similar transitions in the spectra of penta- and the tetrafluorobenzenes discussed below are also designated *C* bands. The DCS of the *C* bands (see Fig. 11) is forward peaked, permitting us to assign this excitation as singlet → singlet. In pentafluorobenzene, a small peak is apparent with a maximum intensity at approximately 5.85 eV (see Fig. 1). The 6.36 eV transition heavily overlaps this feature and consequently we were not able to obtain a reliable DCS for it. However, the band shape of the transitions between 5.3 and 7.5 eV is approximately independent of angle, indicating that the DCS curves of the three transitions in this energy-loss region are quite similar. Therefore, we may assign the 5.85 eV feature to a singlet → singlet excitation. We believe that this transition is analogous to the feature observed in the hexafluorobenzene spectrum at 5.32 eV (*C* band). With decreasing fluorine substitution, the *C* band apparently shifts to higher energy loss.

Analysis of the 5.5–7.0 eV region of the tetrafluorobenzene spectra is quite complicated. In 1,2,3,4-tetrafluorobenzene, there is a definite broadening on the low-energy side of the 6.43 eV feature ($\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ in benzene notation) and the apparent onset is at lower energy than in molecules with fewer fluorine atoms. This

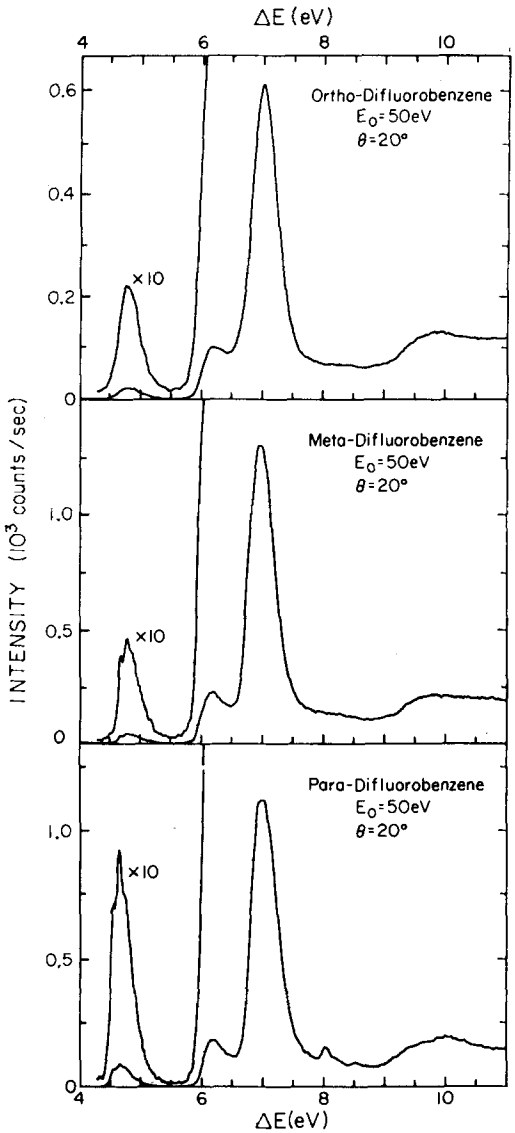

FIG. 3. Electron-impact energy-loss spectra of the difluorobenzenes in the 4 to 11 eV energy-loss region. Experimental conditions are as described in Fig. 1.

broading appears to be due to the superposition of the *C* band (located at 5.85 eV in the penta compound), shifted to even higher energy losses, and the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ excitation. In the 1,2,3,5-tetrafluorobenzene spectra (see Fig. 5), the valley between the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ and $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ transitions which is observed in the 1,2,3,4-tetrafluorobenzene spectra (at 6.43 and 7.21 eV, respectively) is not visible, indicating that the *C* band has shifted to somewhat higher excitation energy, approximately 6.4 eV. The spectrum of 1,2,4,5-tetrafluorobenzene also lacks the valley between the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ and $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ transitions and, in addition, displays a slope break on the low-energy side of the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ excitation. This slope break is more apparent in spectra obtained at 30 eV impact energy and occurs at approximately 6.9 eV. Whether it is due to the superposition of the *C* band singlet → singlet feature observed in hexa-, penta-, and 1,2,3,4-tetrafluorobenzene and the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ transition, or is the result of an entirely different excitation is not obvious.

B. The nature of the *C* band

The *C* band singlet state observed in hexafluorobenzene at 5.32 eV and higher energy losses in the penta- and tetrasubstituted molecules has also been observed in the hexafluorobenzene optical spectrum.[40] However, the character of this transition has been explicitly discussed only in our preliminary description of these fluorobenzene results.[41] One possibility is that the *C* band transitions may be related to the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{2g}^-$ [18,19] transition of benzene. In hexafluorobenzene, the excitation energy of the *C* band is near that of a weak vibronic system observed by Taleb *et al.*[42] and Morris and Angus,[43] who studied absorption and photoexcitation spectra, respectively, of benzene in rare gas matrices. The intensity maximum of this transition in the absorption spectrum[42] was located at approximately 5.77 eV and assigned to the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{2g}^-$ [44] excitation. Two points should be considered when analyzing the possible relationship of this transition in benzene to the *C* bands in the fluorobenzenes. First, the possibility exists that these vibronic peaks in the matrix spectra are due to impurities. Relative to the intensity of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ transition, these $^1E_{2g}^-$ bands are at least ten times more intense in the absorption spectrum of Taleb *et al.*[42] obtained using a perfluoro-*n*-hexane solvent at −85 °C than in the krypton film spectrum of Morris and Angus.[43] In addition, this feature is not observed at all in the vapor phase, high resolution electron-impact spectrum of benzene obtained by Lassettre *et al.*[13] Secondly, assuming that the supposed $^1E_{2g}^-$ bands are indeed due to benzene,

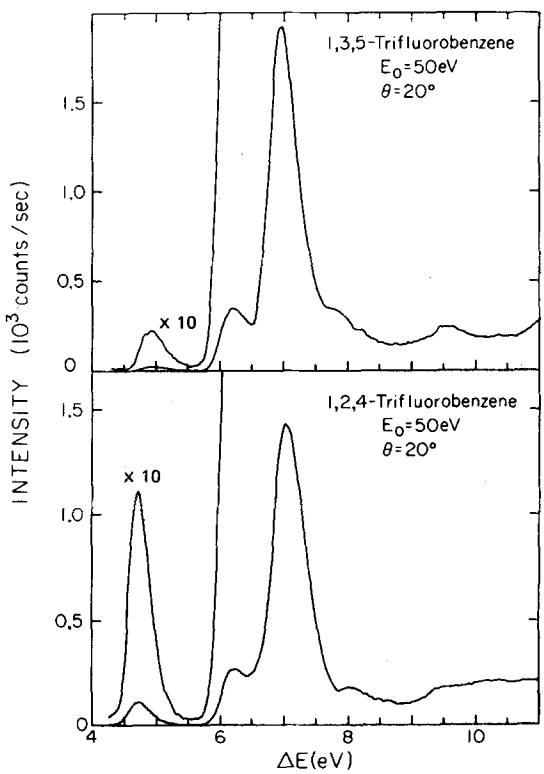

FIG. 4. Electron-impact energy-loss spectra of 1,3,5-trifluorobenzene and 1,2,4-trifluorobenzene in the 4 to 11 eV energy-loss region. Experimental conditions are as described in Fig. 1.

their valence assignment is inconsistent with the relatively large downward shift of 0.5 eV in the observed excitation energy of the *C* band in going from penta- to hexafluorobenzene when compared with those of the other valence singlet states. We conclude that the 5.77 eV excitation in the spectra of benzene in rare gas matrices does not correspond to the *C* band in the fluorobenzenes.

The *C* bands also seem not to be related to the transitions observed by Johnson[17] and Lassettre *et al.*[13] in the 6.3 to 6.7 eV energy-loss region (see Sec. II). If these excitations are valence transitions within the phenyl ring, then the excitation energy behavior with varying fluorine substitution of the *C* bands is again inconsistent with this proposed assignment because of the relatively large shift between the penta and hexa compounds. The likelihood that the *C* bands are of the Rydberg type also appears to be small. The vertical ionization potentials of pentafluorobenzene and hexafluorobenzene are both 10.1 eV.[45] If the *C* bands are Rydberg-like, there should be a negligible difference in the corresponding excitation energies in these two molecules since the respective quantum defects should be approximately equal.

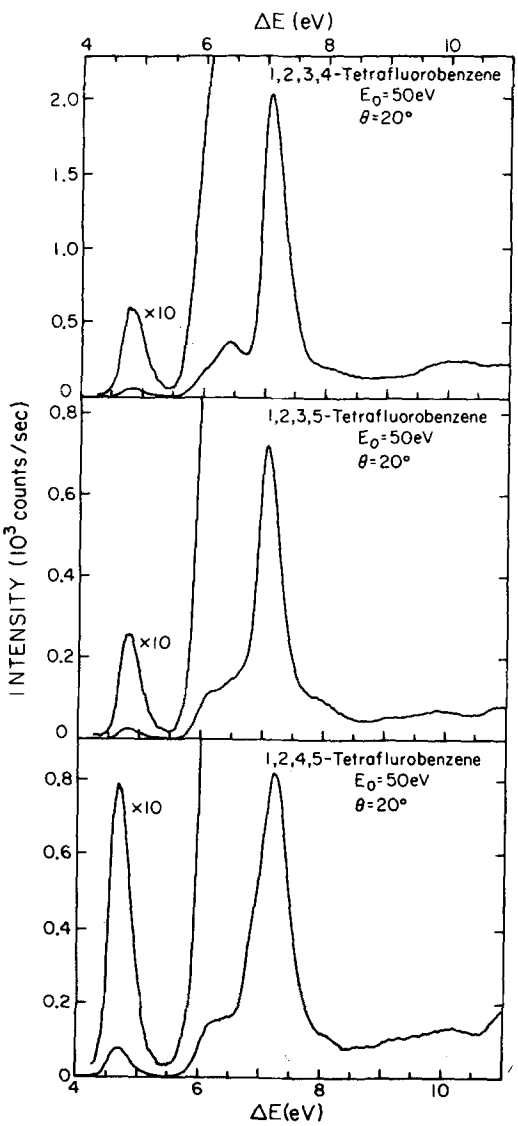

FIG. 5. Electron-impact energy-loss spectra of the tetrafluorobenzenes in the 4 to 11 eV energy-loss region. Experimental conditions are as described in Fig. 1.

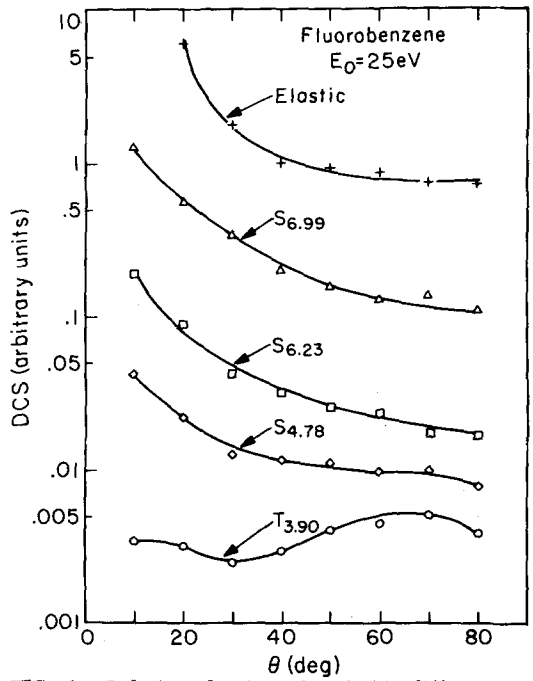

FIG. 6. Relative elastic and inelastic differential cross sections for fluorobenzene at an incident electron energy of 25 eV. These differential cross sections are in arbitrary units set by normalizing the elastic differential cross section to 1.0 at $\theta = 40°$. The arbitrary units are the same for all transitions of a given molecule at a particular impact energy. The arbitrary units are not the same for different molecules or for the same molecule at different impact energies.

Still another possibility is that this 5.32 eV singlet → singlet transition involves an interaction of the fluorine

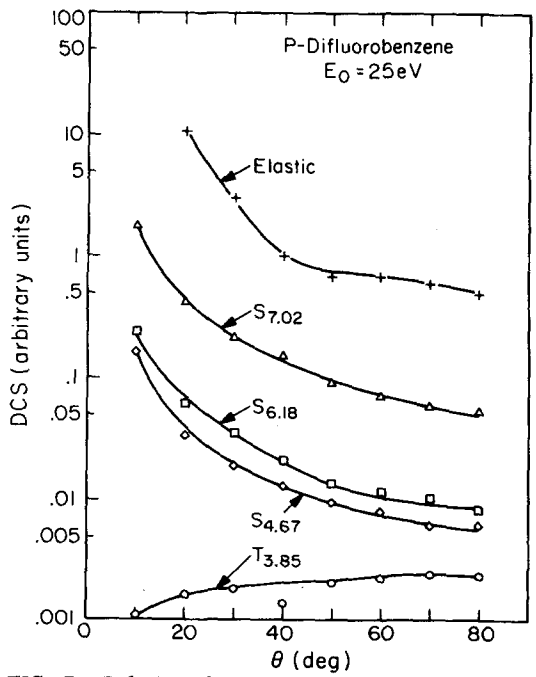

FIG. 7. Relative elastic and inelastic differential cross sections for *p*-difluorobenzene at an incident electron energy of 25 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 6.

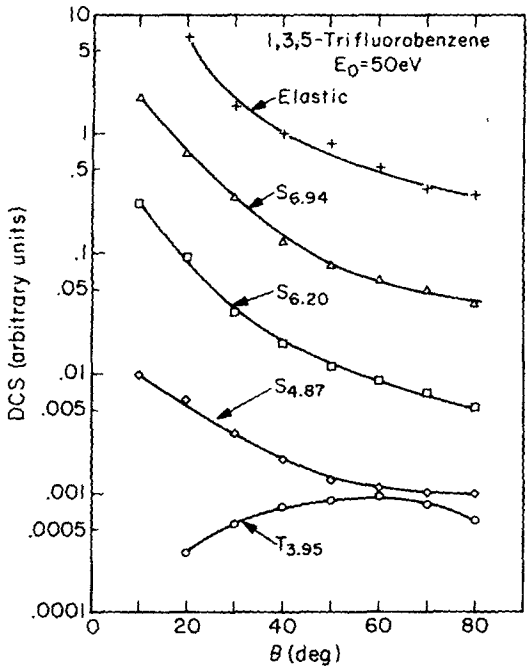

FIG. 8. Relative elastic and inelastic differential cross sections for 1, 3, 5-trifluorobenzene at an incident electron energy of 50 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 6.

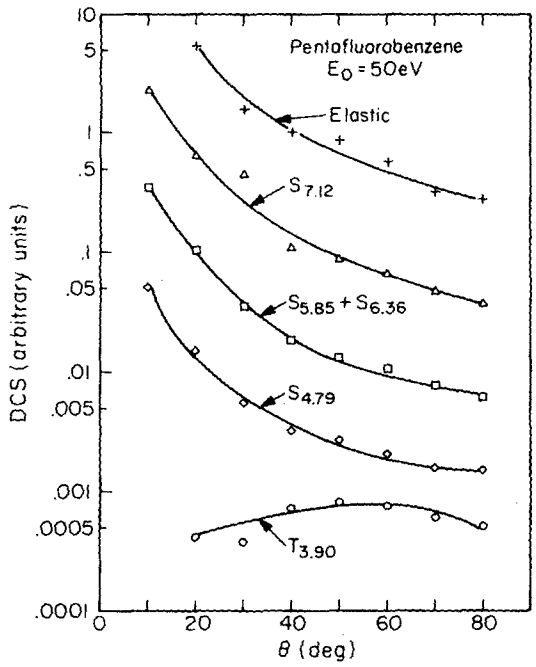

FIG. 10. Relative elastic and inelastic differential cross sections for pentafluorobenzene at an incident electron energy of 50 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 6.

substituents with the benzene ring. Two types of transitions of this kind appear to be plausible, in the sense of being able to explain the observed shifts in transition energy as the degree of fluorine substitution increases. The first may be described as a charge-transfer transition involving excitation of a fluorine p_π electron to a carbon p_{π^*} orbital. Kimura and Nagakura[28] have found significant differences between the optical spectrum of benzene and those of other monosubstituted benzenes (e.g., –I, –Br, and –SH), involving changes in excitation energies and the appearance of additional electronic bands. They felt that charge-transfer configurations were im-

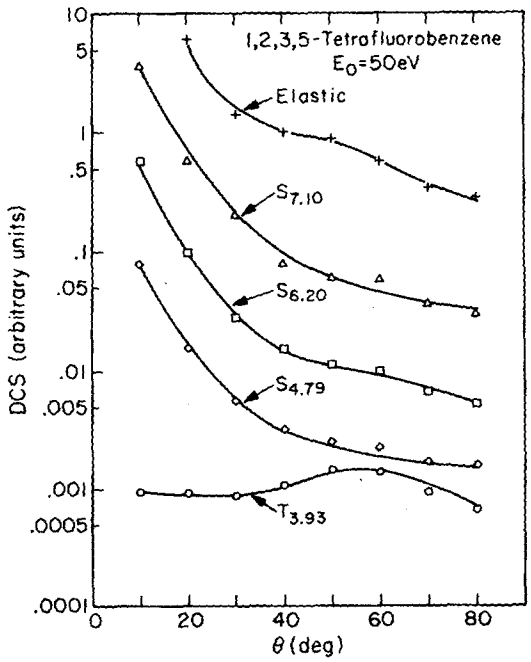

FIG. 9. Relative elastic and inelastic differential cross sections for 1, 2, 3, 5-tetrafluorobenzene at an incident electron energy of 50 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 6.

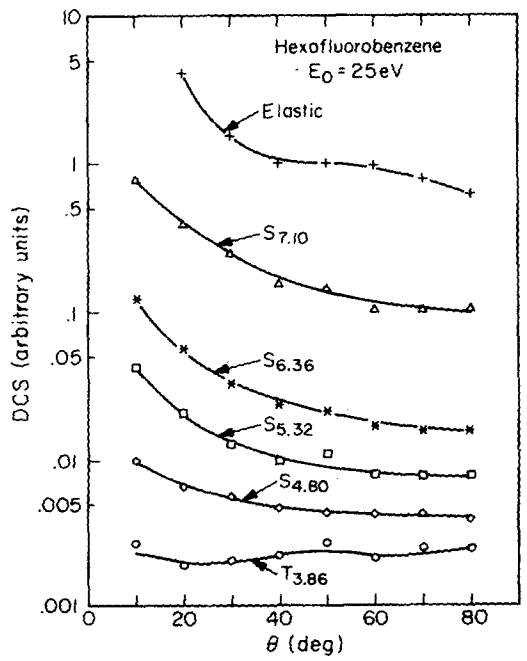

FIG. 11. Relative elastic and inelastic differential cross sections for hexafluorobenzene at an incident electron energy of 25 eV. The normalization procedure for the arbitrary ordinate units is the same as for Fig. 6.

portant in a description of the excited states responsible for the extra bands. A discussion of the expected effect of charge transfer on the variation of *C* band transition energies with fluorine substitution is given below.

A second type of excitation involving a halogen substituent was discussed by Mulliken,[46] who suggested that the longest wavelength bands of the alkyl bromides and iodides are probably due to an $n_{\sigma_X} \rightarrow \sigma^*_{C-X}$ (X = Br and I), $\sigma^2\pi_x^2\pi_y^2 \rightarrow \sigma^2\pi_x^2\pi_y\sigma^*$ excitation, rather than to a Rydberg transition. Kimura and Nagakura[47] have calculated oscillator strengths, using a simple LCAO technique, for both $n \rightarrow \sigma^*$ and $n \rightarrow$ Rydberg transitions in these molecules. A comparison of these oscillator strengths with experimental values indicates that the $n \rightarrow \sigma^*$ assignment is better than an $n \rightarrow$ Rydberg assignment. Similar bands have been observed in the spectra of chloromethanes.[48] In methylchloride, -bromide, and -iodide, these so-called *A* band transitions are observed at 7.3, 6.2, and 4.8 eV,[49] respectively. Corresponding transitions should therefore be observed in the fluoromethanes in the 7.5 to 12 eV range, but electron-impact studies have not detected them.[50] The reason may be that they are expected to be very weak in these fluorinated molecules.[51] In any event, the existence of $n \rightarrow \sigma^*$ valence transitions in alkyl halides appears likely.

Robin[52] has tentatively assigned an additional transition observed in the hexachlorobenzene spectrum, at 4.71 eV, as the promotion of a chlorine lone-pair electron into the antibonding sigma molecular orbital formed from the chlorine atom and the adjacent carbon atom orbitals. This transition would then be similar to the *A* band transitions observed in haloalkanes. By analogy, a second possible explanation of the *C* band transition observed in the spectra of higher substituted fluorobenzenes is the excitation of a fluorine p_π electron into a C–F σ^* orbital.

Let us now analyze the expected effects of fluorine substitution on the excitation energies associated with the two types of fluorine → ring transitions which we have suggested as possible explanations for the observed *C* bands. We first consider the effects of increasing fluorine substitution on the energy of the orbital into which the fluorine π electron is excited. The σ^* orbital, being localized in the C–F region, should have an energy that is relatively independent of the presence of adjacent fluorines. The variation of the π^* orbital energy with substitution will probably be similar to that of the π orbital, since they occupy similar spatial regions and differ primarily in their nodal pattern.[18] On the basis of an analysis of ionization potentials, the highest π molecular orbital in these molecules is found to be stabilized by less than 1 eV when fluorine substitution is increased from benzene to hexafluorobenzene.[35] As a result, the lowest π^* orbital energy will probably also be relatively independent of fluorine substitution.

Turning now to the effects of fluorine substitution on the energy of the fluorine p_π orbital, we note that the shifts in charge resulting from the fluorine interactions with the ring are of two primary types: the inductive effect of the fluorine through the σ bond, and a back migration of the p_π electron density toward the ring.[12,24] As the fluorine p_π density is back donated, there will be a repulsive electrostatic interaction between the fluorine p_π's and the ring p_π's. This should tend to destabilize the fluorine π orbitals. In addition, the fluorine π and the ring π orbitals are both doubly occupied. The Pauli principle forces these orbitals to remain orthogonal, further raising the orbital energy of the fluorine π orbitals.

With increasing fluorine substitution, this destabilizing interaction should become increasingly important as the carbon p_π orbitals are less able to recede from the encroaching fluorine p_π orbitals. In pentafluorobenzene, for example, the carbon p_π cloud should be able to move outward, away from the fluorine clouds, along approximately one third of the periphery of the ring. However, upon substitution of the sixth fluorine, the freedom of in-plane distortion is eliminated. When this occurs, one would expect a sudden increase in the fluorine p_π orbital energies which might account for the 0.5 eV decrease in the transition energy of the *C* band.

The tetrafluorobenzene isomers are also interesting molecules to consider. In all of them, the fluorine p_π orbitals should be less affected by the electrostatic interactions and orthogonality constraints considered above than in pentafluorobenzene. This should result in higher *C* band excitation energies. Such a shift in excitation energy appears indeed to be observed, as can be seen from Table I and Figs. 1 and 5. In 1,2,3,4-tetrafluorobenzene, the carbon π system should be able to distort along nearly one half of the benzene ring, while in the 1,2,3,5- and 1,2,4,5-isomers, this angular region of distortion should be close to 240°. It would be expected, on this basis, that the *C* band in 1,2,3,4-tetrafluorobenzene should occur at a somewhat lower excitation energy than in the two other tetra isomers. Since the relative intensities of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ benzene-type transition and the *C* band are approximately the same in the penta and hexa compounds, we would expect their ratios not to change significantly for the tetra compounds, and to be approximately the same for all three isomers considered. Comparison of the energy-loss region between 5.5 and 6.5 eV in the spectra of each of these tetra isomers (see Fig. 5) shows an obvious difference between the shape of the absorption in 1,2,3,4- and those of the two other tetra isomers. We attribute the shape of the 1,2,3,4-tetrafluorobenzene spectrum in this region to the superposition of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ excitation at 6.43 eV and the *C* band, which appears to have a maximum intensity located at about 6 eV. In the other tetra isomers, on the other hand, the *C* band has apparently shifted to somewhat higher energies (6.4 to 6.5 eV), whereas the maximum of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$ benzene-type transition seems to have shifted to somewhat lower energies (6.2 to 6.3 eV). This reversal of the order of the *C* band and the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{1u}$-like transition energies is consistent with both the analysis of electron orbital distortions just given, as well as with the assumption that the relative intensities of these two transitions are fairly independent of isomeric configuration.

In summary, the exact nature of the *C* bands is not known. They appear not to be related to transitions

TABLE II. Comparison between electron-impact and optical allowedness of $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ transition.

Molecule	Molecular point group	Excited state symmetry	Transition symmetry allowed?	f/f_B f = optical oscillator strength	R/R_B[a] ($\cong f^{EI}/f_B^{EI}$)	R/R_{HFB}[a] ($\cong f^{EI}/f_{HFB}^{EI}$)
Benzene	D_{6h}	B_{2u}	No	1.0[b,c]	1.0	0.8
Fluorobenzene	C_{2v}	B_1	Yes	5.6[b]	2.5	2.1
o-Difluorobenzene	C_{2v}	B_1	Yes		3.6	3.0
m-Difluorobenzene	C_{2v}	B_1	Yes	6.0[b]	2.0	1.7
p-Difluorobenzene	D_{2h}	B_{3u}	Yes	14.0[b,c]	7.3	6.1
1,3,5-Trifluorobenzene	D_{3h}	A_1'	No	1.3[b]	0.7	0.6
1,2,4-Trifluorobenzene	C_s	A'	Yes	12.0[b]	5.7	4.8
1,2,3,4-Tetrafluorobenzene	C_{2v}	B_1	Yes	3.9[d]	3.6	3.0
1,2,3,5-Tetrafluorobenzene	C_{2v}	B_1	Yes	4.2[d]	2.6	2.2
1,2,4,5-Tetrafluorobenzene	D_{2h}	B_{3u}	Yes	15.0[d]	7.3	6.1
Pentafluorobenzene	C_{2v}	B_1	Yes		2.7	2.3
Hexafluorobenzene	D_{6h}	B_{2u}	No	1.9[e]	1.2	1.0

[a] R is the ratio of the area of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$-type transition (in benzene notation) to the area of the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$ transition at $\theta = 10°$ and $E_0 = 50$ eV for the molecule being considered. R_B and R_{HFB} are the equivalent ratios for benzene and hexafluorobenzene, respectively. f^{EI} is the electron-impact generalized oscillator strength for the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$-type transition for the molecule being considered, and the f_B^{EI} and f_{HFB}^{EI} are the corresponding oscillator strengths in benzene and hexafluorobenzene, respectively.

[b] Ratios obtained from optical data presented in Ref. 12.

[c] Although more recent values of f, based on electron-impact measurements, exist for benzene and *p*-difluorobenzene [K. N. Klump and E. N. Lassettre, Chem. Phys. Lett. 51, 99 (1977); J. Chem. Phys. 68, 3511 (1978)], we have used only optical data for consistency with the other molecules.

[d] Tetrafluorobenzene oscillator strength estimated from the optical spectrum in Ref. 9.

[e] Hexafluorobenzene oscillator strength estimated from the optical spectrum in Ref. 40.

among benzene ring-type orbitals. They do, on the other hand, seem to be associated with fluorine orbitals. The variation of the *C* band transition energy with the number of fluorine substituents as well as their isomeric configurations seems to be consistent with either a charge transfer excitation, i.e., fluorine p_π to carbon p_{π^*}, or a fluorine p_π to C–Fσ^* transition. It is clear that further experimental and theoretical work is required to identify the *C* band.

C. Comparison between electron-impact and optical intensities of the transitions analogous to the benzene $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ excitation

Study of the fluorobenzenes allows determination of the effects of varying molecular symmetry on the relative intensities of transitions in electron-impact spectra. As mentioned above, the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$ excitation in benzene is symmetry forbidden and is observed in optical spectra due to vibronic interactions.[1] In the fluorobenzene series investigated here, the analogous transition is symmetry forbidden for only two other molecules besides benzene: 1,3,5-trifluorobenzene and hexafluorobenzene. In Table II, we display the optical oscillator strengths for these transitions relative to the one in benzene (f/f_B) for the entire fluorobenzene series. We also display the R/R_B and R/R_{HFB} quotients, where R is the ratio of the integrated electron impact intensity of the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$-type transition to that of the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_u$-type transition (in benzene notation), while R_B and R_{HFB} are the values of this ratio for benzene and hexafluorobenzene, respectively.

For our experimental conditions, it turns out that these quotients of R values are approximately equal to corresponding quotients of generalized oscillator strength values. More specifically, let f^{EI} be the electron-impact generalized oscillator strength for the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$-type transition of a given fluorobenzene, and let f_B^{EI} and f_{HFB}^{EI} be the oscillator strengths for benzene and hexafluorobenzene, respectively. The property which is valid under our conditions is that f^{EI}/f_B^{EI} and f^{EI}/f_{HFB}^{EI} are approximately equal to R/R_B and R/R_{HFB}, respectively. This is so on the basis of three facts: (a) The integrated electron-impact intensities for the $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$-type transitions in benzene and the fluorobenzenes used to determine the values of R, R_B, and R_{HFB} involved in Table II were obtained from spectra all of which were taken at the same impact energy (50 eV) and scattering angle (10°). (b) The shapes of the corresponding DCS versus scattering angle curves, at this impact energy, were nearly the same for all molecules and both transitions being considered. (c) The $\tilde{X}\,^1A_{1g} \rightarrow {}^1E_{1u}$-type transition is optically allowed in benzene and in all of its fluorinated derivatives, and the corresponding optical oscillator strengths are all approximately equal[24] (~1.1). The property being considered is an immediate consequence of these facts and of the definition of generalized oscillator strength.[53]

The optical oscillator strength ratios (f/f_B) in the three molecules for which the $\tilde{X}\,^1A_{1g} \rightarrow 1\,^1B_{2u}$-type transition is symmetry forbidden are significantly smaller than those in the molecules for which it is symmetry allowed, as can be seen from Table II. It is interesting to analyze the corresponding relative intensities in the electron-impact spectra. Rigorously speaking, these electron-impact transition intensities will only obey dipole selection rules when the Born approximation is

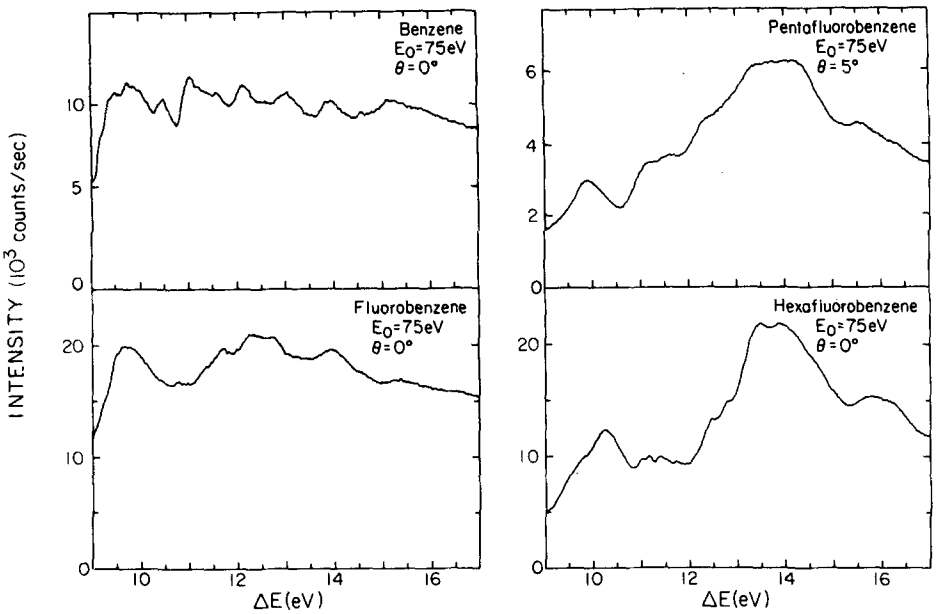

FIG. 12. Electron-impact energy-loss spectra of benzene, fluorobenzene, pentafluorobenzene, and hexafluorobenzene in the 9 to 17 eV energy-loss region. Experimental conditions are as described in Fig. 1.

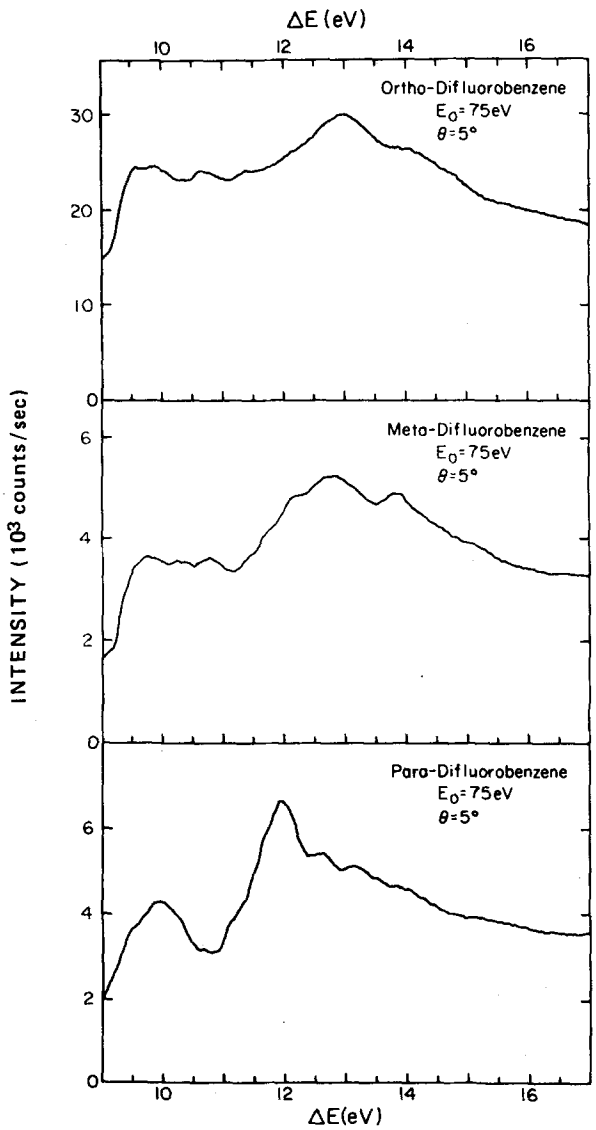

FIG. 13. Electron-impact energy-loss spectra of the difluorobenzenes in the 9 to 17 eV energy-loss region. Experimental conditions are as described in Fig. 1.

valid. This occurs for small values of the ratio $\Delta K/K$ of the momentum transfer ΔK to the incident electron momentum K, such as those which occur at high incident electron energies and low scattering angles.[53,54] As indicated above, we are considering the intensity variation with fluorine substitution of the first singlet → singlet transition in the fluorobenzenes for spectra taken at an impact energy of 50 eV and a scattering angle of 10°.[55] We chose these parameters to minimize any contribution due

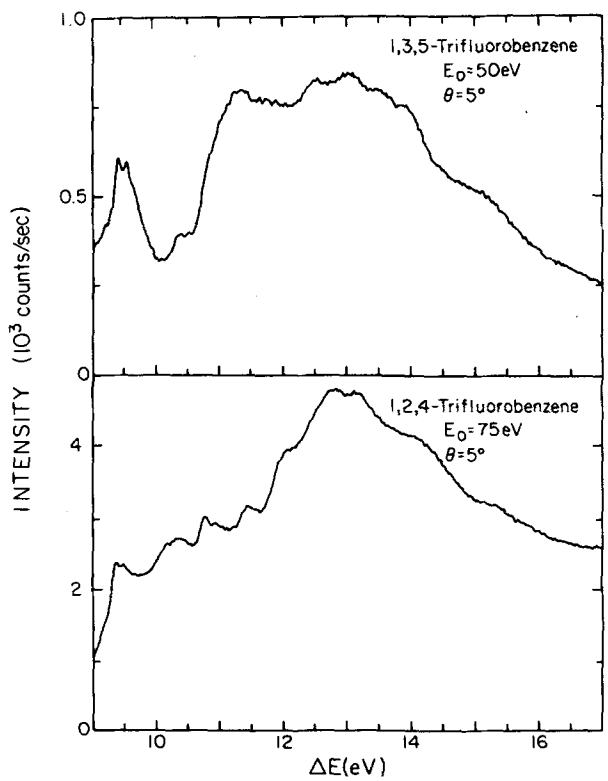

FIG. 14. Electron-impact energy-loss spectra of 1, 3, 5-trifluorobenzene and 1, 2, 4-trifluorobenzene in the 9 to 17 eV energy-loss region. Experimental conditions are as described in Fig. 1.

TABLE III. Transition energies in eV from ground to excited electronic states of the fluorobenzenes in the energy-loss region above 8 eV.[a]

Benzene	Fluoro-benzene	*o*-Difluoro-benzene	*m*-Difluoro-benzene	*p*-Difluoro-benzene	1,3,5-$C_6H_3F_3$	1,2,4-$C_6H_3F_3$	1,2,3,4-$C_6H_2F_4$	1,2,3,5-$C_6H_2F_4$	1,2,4,5-$C_6H_2F_4$	C_6HF_5	C_6F_6
8.14	8.87	8.14	7.94	8.04	8.20	8.13	8.13	9.07	8.07	9.91	9.82
8.41	9.73	8.46	8.28	8.50	8.56	8.52	8.43	9.92	8.26	11.11	10.26
8.72	10.75	9.60	8.46	9.49	8.73	9.18	9.05	11.02	8.59	11.61	10.99
8.88	11.38	9.93	9.06	9.98	9.43	9.42	9.90	11.82	9.14	12.35	11.14
9.50	11.72	10.73	9.78	11.13	9.56	9.53	10.40	12.62	10.16	13.41	11.39
9.76	12.33	11.39	10.31	11.98	10.40	10.23	10.90	13.06	11.06	14.25	11.72
9.90	12.73	12.13	10.79	12.67	11.33	10.40	11.91	14.00	12.39	15.58	12.49
10.01	13.93	12.99	11.76	13.23	12.51	10.83	12.58	15.32	13.26	16.40	12.79
10.51	14.63	14.09	12.21	14.03	13.08	10.98	13.08	16.00	13.64		13.46
11.08	15.27		12.84	15.40	13.55	11.40	13.58		13.96		13.89
11.61	16.97		13.84		13.96	11.50	14.33		14.49		15.81
12.15			15.31		15.16	11.62	15.50		15.62		18.32
13.08			17.01			12.13	16.31				
13.96						12.90	17.21				
14.26						13.20					
15.21						14.30					
15.81						15.47					
17.45						17.47					

[a]The accuracy in the location of the peaks of the reported transitions is ±0.05 eV.

to the triplet state which underlies the low-energy region of the singlet state excitation. The quantity R/R_B, which we have found to be approximately equal to f^{EI}/f_B^{EI}, is an appropriate one for comparison with the corresponding ratio (f/f_B) of optical oscillator strengths. It can be seen from the values of R/R_B in Table II that, as in the optical spectra, the dipole-allowed transitions are relatively more intense than the dipole-forbidden excitations in the electron-impact spectra. The differences among the corresponding ratios in column 6 (for the electron-impact spectra) are smaller than those for column 5 (for the optical spectra), indicating that, at 50 eV impact energies, dipole selection rules are somewhat relaxed. One expects that these ratios will gradually approach the optical values as the impact energy increases.

Finally, we compare the electron-impact ratios of pairs of molecules which are related to one another by the replacement of fluorines by hydrogens and *vice versa*, such as fluorobenzene and pentafluorobenzene. For this pair of molecules, the appropriate comparison is between the f^{EI}/f_B^{EI} ratio for the first of these molecules and the f^{EI}/f_{HFB}^{EI} ratio for the second one. Similarly related ratios in columns 6 and 7 of Table II are connected by double-headed arrows. It is seen that the corresponding ratios are close to one another, indicating the importance of molecular symmetry, independently of whether the benzene symmetry is broken by F-atom substitution or that of hexafluorobenzene is broken by H-atom substitution.

D. Transitions above 8 eV

We have obtained electron-impact spectra for excitation energies up to 18 eV. Transitions in the energy region above 8 eV are believed to be primarily due to excitations to Rydberg-like orbitals, forming Rydberg series converging to various ionization potentials. Transitions belonging to series converging to the first ionization potential for several fluorobenzenes have been assigned previously[56–59] on the basis of term values[49,60] as well as vibrational spacings. While assignments of transitions converging to first ionization potentials appear to be reliable, those for transitions converging to higher ionization potentials are less certain. We have been unable to classify uniquely the term values of any of the transitions we observe in the 10 to 18 eV range as being associated with one of the several known ionization potentials of the molecules being considered.[35,45,56–59,61] Spectra of these molecules in the 9 to 17 eV energy-loss range are presented in Figs. 12 through 15. The transition energies of the more prominent excitations above 8 eV are summarized in Table III.

V. SUMMARY

We have investigated the electronic spectra of benzene and 11 of its fluorine-substituted derivatives. In each molecule, the location and Franck–Condon envelope of the lowest triplet state has been accurately determined. In fluorobenzene, *o*- and *m*-difluorobenzene, and 1,3,5-trifluorobenzene, a second triplet, apparently analogous to the $1\,^3B_{2u}$ state of benzene, was detected. Each of the fluorobenzenes studied has three singlet → singlet transitions that are analogous to the well-known features in the benzene spectra at 4.90, 6.20, and 6.95 eV. An additional spin-allowed transition, which we have designated the *C* band system, is observed in 1,2,3,4-tetrafluorobenzene at about 6.0 eV as a broadening on the low-energy side of the 6.43 eV feature. In the other two tetrafluorobenzenes, it appears to occur at the slightly higher energy loss of about 6.4–6.5 eV. This transition is more clearly observed in the spectra of pentafluorobenzene and hexafluorobenzene, with a maximum intensity at 5.85 and 5.32 eV, respectively. The identity of this transition is uncertain, but the dependence of its transition energy on in-

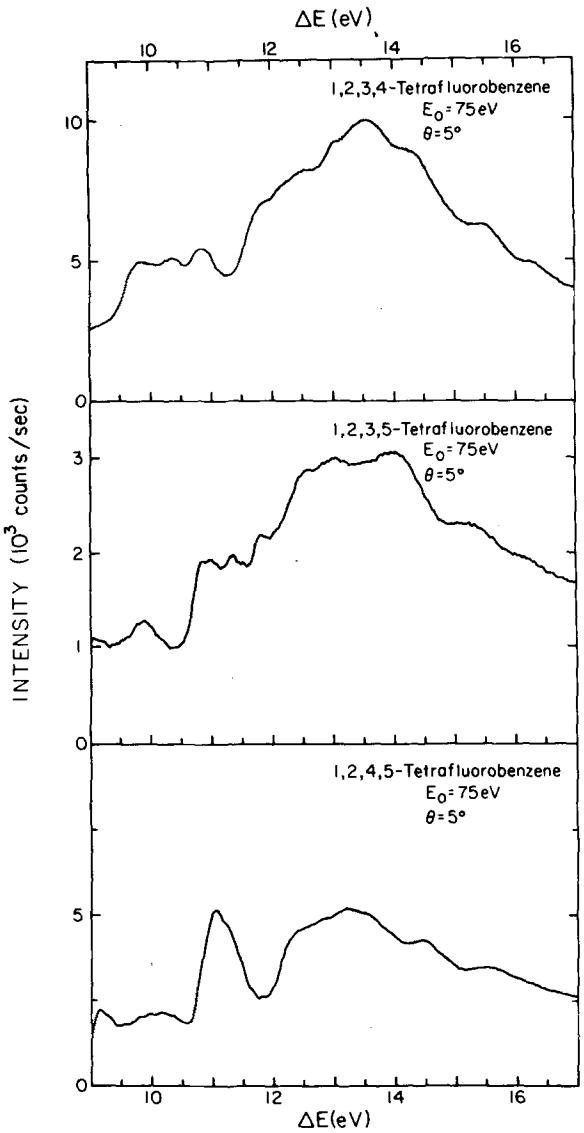

FIG. 15. Electron-impact energy-loss spectra of the tetrafluorobenzenes in the 9 to 17 eV energy-loss region. Experimental conditions are as described in Fig. 1.

creasing fluorine substitution is best rationalized by assigning it to a charge-transfer $F_{p_\pi} - C_{p_{\pi^*}}$ excitation or to an $F_{p\pi} - C - F_{\sigma^*}$ transition.

The dependence on molecular symmetry of the lowest singlet – singlet transition intensity in the several fluorobenzene spectra was discussed. Dipole selection rules were found to be obeyed less rigorously in the electron-impact spectra than in the corresponding optical spectra. Finally, numerous transitions at high excitation energies, including transitions to superexcited states, were observed. These are believed to be primarily transitions to Rydberg-like orbitals.

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[38]There are few exceptions to the rule that sharply forward-peaked transitions are spin-allowed. These exceptions, however, are for atoms or diatomic molecules.[2] For the polyatomic molecules studied so far, no such exceptions exist, to the best of our knowledge.

[39]For simplicity, we will hereafter refer to this band system as the *C* band. The letter *C* is arbitrary, chosen to avoid confusion with the *A*-, *B*-, and *E*-type irreducible representations of the D_{6h} point group.

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